



**US Army Corps
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Engineer Research and
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Environmental Security and Technology Certification Program

Biopolymers as an Alternative to Petroleum- Based Polymers for Soil Modification

ESTCP ER-0920: Treatability Studies

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August 2012

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Final report

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Abstract

Rhizobium tropici, a catalogued symbiotic nodulator of leguminous plants, is also known for its production of a gel-like extracellular polymeric substance (EPS). The natural functions of the biopolymer in the rhizosphere include surface adhesion, self-adhesion of cells into biofilms, formation of protective barriers, water retention around roots, and nutrient accumulation. We performed three treatability studies to evaluate the effectiveness of the biopolymer as a soil amendment to increase slope stability and reduce transport of solids in runoff water, reduce the transport of heavy metals associated with suspended sediment from small arms firing ranges, and reduce the generation of dust. Four soil types were used: Silty Sand (SM), Sandy Silt (ML), Silt (S), and Silty Clay (CL). These soil types were selected because they are prone to wind and water erosion thus presenting possible worst case scenarios. The study of sediment transport demonstrated that the biopolymer soil amendment was able to significantly reduce surface water erosion and particulate and heavy metal transport in leachate. The biopolymer soil amendment effectively maintained the slope stability of a simulated berm. In addition, biopolymer added to the Silty Sand soil at 0.5% (w:w) loading rate reduced dust production compared to the control at all relative humidities, indicating it should perform well in both arid and tropical environments.

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Contents

Abstract.....	ii
Figures and Tables.....	v
Preface.....	vi
Acronyms	vii
1 Introduction.....	1
Biopolymer.....	1
Slope stability and erosion control	5
Metal migration	6
Fugitive dust emissions.....	8
2 Experimental Design.....	11
Objectives	11
<i>Slope stability and erosion control</i>	<i>11</i>
<i>Metal migration.....</i>	<i>11</i>
<i>Fugitive dust emissions</i>	<i>11</i>
Experimental design.....	11
<i>Slope stability and erosion control</i>	<i>11</i>
<i>Metal migration.....</i>	<i>12</i>
<i>Fugitive dust emissions</i>	<i>12</i>
3 Materials and Methods.....	13
Materials.....	13
<i>Experimental soils</i>	<i>13</i>
<i>Biopolymer amendment</i>	<i>13</i>
<i>Slope stability boxes</i>	<i>13</i>
<i>Mesoscale rainfall lysimeters.....</i>	<i>13</i>
<i>Live-fire lysimeters (LFL).....</i>	<i>15</i>
<i>Dust palliative spray device.....</i>	<i>16</i>
Methods.....	17
<i>Slope stability boxes</i>	<i>17</i>
<i>Mesoscale rainfall lysimeters.....</i>	<i>17</i>
<i>Live-fire lysimeter.....</i>	<i>17</i>
<i>Firing specifications</i>	<i>17</i>
<i>Weathering and sampling.....</i>	<i>18</i>
<i>Fugitive dust emissions</i>	<i>18</i>
<i>Sample analysis</i>	<i>19</i>
4 Results and Discussion.....	20
Slope stability and erosion control	20
<i>Soil loss.....</i>	<i>20</i>

<i>Sediment load in runoff</i>	21
Heavy metals in leachate and runoff water	23
Fugitive dust emissions.....	27
5 Conclusions	29
Slope stability and erosion control	29
Metal migration	29
Fugitive dust emissions.....	30
References	31
Report Documentation Page	

Figures and Tables

Figures

Figure 1. Comparison of FT-IR spectra of carbon sources used as feedstock for the production of EPS from <i>R. tropici</i>	4
Figure 2. a) The polymerization reaction of the biopolymer, b) Highlighting the cross-linking reaction through the formation of covalently bonded amide linkages.	5
Figure 3. GPC evaluation of the of the <i>R. tropici</i> biopolymer salt grown using different carbon sources as feedstock.	5
Figure 4. Slope stability boxes with-unamended control cells on left and 0.2% biopolymer cells on right. The soil types in each pair are Silty Sand on left and Silt on right. Note the clarity of the leachate water from the biopolymer-amended soils on the right.	14
Figure 5. Mesoscale rainfall lysimeter.....	14
Figure 6. A live-fire lysimeter cell.....	15
Figure 7. Photographs illustrating the upper and lower leachate and surface water collection systems in the extended toe LFL.	16
Figure 8. Mass lost by soil type and biopolymer loading rate.	20
Figure 9. Illustration of the surface durability and resistance to erosion of biopolymer amended soil over the untreated control.....	21
Figure 10. Comparison of TSS in runoff water and leachate from control and biopolymer-amended Silty Clay soil during the slope stability studies as run in the static mesoscale lysimeter systems.	22
Figure 11. Total suspended solids in runoff water and leachate from untreated and biopolymer-amended metals-contaminated soil in the live fire lysimeter after 1.25 yr simulated weathering.	22
Figure 12. Mass of total lead in runoff water and leachate from untreated and biopolymer-amended metals-contaminated soil after 1.25 year of simulated weathering using the static mesoscale rainfall lysimeter.....	24
Figure 13. Mass of total lead (Pb) in the upper leachate from soil amended with biopolymer from molasses-derived carbon feedstocks.....	26
Figure 14. Mass of total lead (Pb) in the lower leachate from soil amended with biopolymer from the molasses-derived feedstock.	26
Figure 15. Comparison of mass loss from Silty Sand soil treated with biopolymer at three loading rates and three relative humidities.	27

Tables

Table 1. USEPA Air Quality Standards for Particulate Matter	9
Table 2. Lysimeter cell and amendment.....	16
Table 3. Weapon specifications for the live-fire lysimeter study.	18
Table 4. The mass of dissolved lead (Pb) in the upper and lower leachate from the control (fired) soil and biopolymer-amended lysimeters following 4 rain events.....	25
Table 5. Biopolymer mass required for a 0.5% application rate for three application depths.	28

Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg. Funding was provided by the Environmental Security Technology Certification Program (ESTCP). The project was designated as ESTCP Project ER-0920.

The work presented in this report was part of an effort to investigate the use of a biopolymer to improve slope stability, decrease erosion, immobilize metals, and reduce the production of fugitive dust on active small arms firing ranges. Dr. Steven L. Larson and Christopher S. Griggs of the ERDC-Environmental Laboratory (EL), Vicksburg, MS, Dr. John K. Newman of the ERDC-Geotechnical and Structures Laboratory (GSL), Vicksburg, MS, Milton Beverly of Environmental Research and Development, Inc. (ERD), Vicksburg, MS, and Catherine C. Nestler of Applied Research Associates, Inc. (ARA), Vicksburg, MS, prepared this report. The report was reviewed by Deborah Felt and Dr. Heather Knotek-Smith of ERDC-EL. The authors gratefully acknowledge the technical assistance provided by Catherine Thomas (Jackson State University) and Debraka Williams (Alcorn State University).

This study was conducted under the direct supervision of W. Andy Martin, Branch Chief (EP-E); and Warren Lorentz, Division Chief (EP); and under the general supervision of Dr. Patrick Deliman, Technical Director (EL) and Dr. Elizabeth Ferguson, Technical Director (EL).

At the time of publication of this report, Dr. Beth Fleming was the EL Director; COL Richard B. Jenkins was Commander and Executive Director of ERDC; Dr. Jeffrey Holland was Director of ERDC.

Acronyms

BMP	Best management practice
BP	Biopolymer
CL	Clay
Da	Dalton, unit of molecular weight
EPA	Environmental Protection Agency
EPS	Extracellular polymeric substance
ERDC	Engineer Research and Development Center
FT-IR	Fourier transform – Infrared
GPC	Gel permeation chromatography
ICP	Inductively-coupled plasma
LFL	Live-fire lysimeter
ML	Sandy Silt
NAAQS	National Ambient Air Quality Standards
NOM	Natural Organic Matter
PM	Particulate Matter
S	Silt
SAFR	Small Arms Firing Range
SM	Silty Sand

TSS	Total suspended solids
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Chemical Nomenclature

Sb	Antimony
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As	Arsenic
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CO	Carbon monoxide
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Cr	Chromium
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Cu	Copper
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Fe	Iron
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Pb	Lead
----	------

Mn	Manganese
----	-----------

Mo	Molybdenum
----	------------

Ni	Nickel
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NO _x	Nitrogen oxides
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O ₃	Ozone
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SO ₂	Sulfur dioxide
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V	Vanadium
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Zn	Zinc
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1 Introduction

Biopolymer

Rhizobium tropici ATCC® 49672, a catalogued symbiotic nodulator of leguminous plants (Martinez-Romero et al. 1991), is also known for its production of a gel-like extracellular polymeric substance (EPS) (Gil-Serrano et al. 1990). Most of the *Rhizobium*-produced EPS are polysaccharides containing glucuronic acid (Dudman et al. 1983a, 1983b, Franzen et al. 1983), although some exceptions to this structure have been reported (Amemura and Harada 1983, Gil-Serrano et al. 1990). Studies of the structure of these polymers have been reviewed by Laspidou and Rittmann (2002). The natural functions of the EPS in the rhizosphere include surface adhesion, self-adhesion of cells into biofilms, formation of protective barriers, water retention around roots, and nutrient accumulation (Laspidou and Rittmann 2002).

Secretion of EPS by bacteria is recognized as a cohesive force in promoting surface erosion resistance in sediments (Droppo 2009, Gerbersdorf et al. 2008a, 2008b). EPS studied in the marine environment have been demonstrated to be a significant factor in marine geochemistry and an important alternate route of organic carbon cycling (Bhaskar and Bhosle 2005). The function of bacterial EPS in promoting soil adhesion has also been reported for several cyanobacteria in arid environments (Hu et al. 2003). Soil modification using the natural products of indigenous soil bacteria has introduced the concept of biogeocivil engineering (Jonkers and Loosdrecht 2010).

The adhesive, water retention, and protective biofilm formation qualities of the EPS from *R. tropici* are reasons for its investigation as a potential soil engineering agent. These characteristics suggest that the *R. tropici* EPS can be used to improve the strength of soil for erosion control and slope stability in situations where traditional techniques, such as geotextiles and vegetative cover, are not applicable.

Numerous products are commercially available for soil strengthening (Tingle et al. 2007). These are all synthetic, petroleum-based soil additives packaged as emulsions. They are gaining popularity due to their ease of handling and lower safety and environmental concerns compared to

traditional soil stabilization agents such as asphalt, cement, and lime. Most soil-stabilizing emulsions are copolymers of ethylene/vinyl acetate or are acrylic copolymers. In some soil types, these additives produce soils with improved engineering properties. Soils mixed with synthetic polymers may exhibit strengths similar to that of cement. However, the polymer mixture imparts more flexibility to the soil than does cement and increases soil toughness. This translates into increased resistance to cracking due to a higher ultimate failure strain before yield (Newman et al. 2005).

Artificial, petroleum-based soil strengthening and stabilizing additives are currently used for erosion control in areas where vegetation and geotextiles are inappropriate, such as testing and training ranges, and dust control in areas where high winds and pressure pulses (natural or artificial) produce dust in quantities that reduce visibility (for example, gun positions and rotary wing landing areas). Heavy metal transport off ranges is a concern with both water and air erosion of soil particulates and requires extensive range maintenance to control. Metals-contaminated dust is a potential health concern for troops. According to Executive Order 13423, "Strengthening Federal Environmental, Energy, and Transportation Management", Energy Independence and Security Act, the U.S. military is currently the nation's single largest consumer of petrochemicals produced from oil. Under DOD Directive 4140.25, "DoD Management Policy for Energy Commodities and Related Services", Pentagon officials put the total energy costs at \$13 billion for 2007 and \$20 billion for 2008. However, petroleum-based polymers can also leach toxic products into the soil (Lentz et al. 2008; Weston et al. 2009) and their production uses a valuable natural resource.

Use of biopolymers reduces the generation of hazardous substances in the design, manufacture, and use of the petroleum-based polymers currently in use as well as the use of petroleum in general. Biopolymers have been shown to be effective alternatives for the petrochemical-based polymer soil additives currently in use. Biologically produced polymers have a number of unique benefits when compared to petrochemical-based polymers, beyond the reduction of chemicals derived from oil. Because biopolymers are produced as a result of complex biosynthesis by bacteria and algae, the polymeric structure is more diversified than the regularly recurring units in traditional plastics. This provides enhanced functionality, including post-application cross-linking, ease of derivatization for specific uses, and a long-lived, but ultimately biodegradable, material without the

environmental concerns associated with synthetic polymers (Cabaniss et al. 2005, Decho 2010, Goto et al. 2001). In addition, use of these materials acts as a carbon storehouse for readily biodegradable sugars that would otherwise be oxidized to carbon dioxide (CO₂) and contribute to elevated greenhouse gasses in the atmosphere.

A technique has been developed through which *R. tropici*-derived biopolymer (BP) can be produced in an aerobic bioreactor. The biopolymer is separated from the growth media and extracted to produce a non-reactive (non-cross-linking) material. This non-reactive material can then be transported as a low-density, dry solid and applied to the soil using one of two methods. The first involves mixing the dry biopolymer with water at the site of use, producing a viscous liquid, or gel, that is applied to the soil surface. The second method involves mixing the dry biopolymer into the soil, then applying water. Using either application method, when wetted, the biopolymer will form a gel within the soil matrix. With the soil acting as a buffer, the ionic character of the biopolymer salt is neutralized and the biopolymer can begin reacting with itself and the constituents of the soil matrix. The reactive, cross-linked biopolymer has a larger molecular weight and a reduced water affinity.

Process modifications have been found that change the biopolymer structure and, therefore, its functionality. Four carbon sources have been tested as feedstock for the production of biopolymer by *R. tropici*: corn syrup, maltose, sorghum, and molasses. The maltose, being a very expensive carbon source, has been replaced by the sorghum. The use of varied carbon sources has been observed to produce biopolymers with varied chemical relativities and functional groups. Physical differences between the biopolymers produced from varied carbon sources included changes in color and texture. Chemical differences were investigated using Fourier transform infrared (FT-IR) and size exclusion, gel permeation chromatography (GPC).

FT-IR with a total attenuated reflectance optical cell was used to evaluate the chemical functionality of three biopolymers, all produced using *R. tropici* and with three separate carbon sources. Figure 1 displays the infra-red spectra of corn syrup, molasses and maltose based biopolymers.

Corn syrup produced similar carboxylic acid content as the maltose-grown material with more alcohol functional groups than observed in the maltose polymer. Corn syrup contains primarily glucose units (Kretchmer and

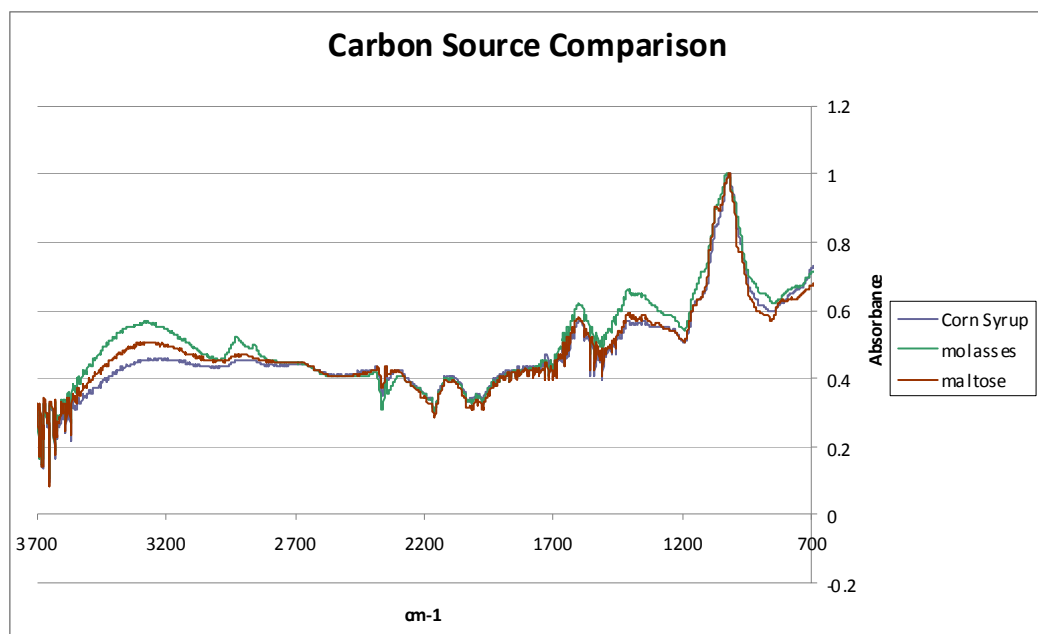


Figure 1. Comparison of FT-IR spectra of carbon sources used as feedstock for the production of EPS from *R. tropici*.

Hollenbeck, 1991). Molasses produced more carboxylic acid groups than the maltose or the corn syrup-based material and approximately the same degree of alcohol functionalization as noted in the corn syrup feedstock biopolymer. The sugars in sugar cane molasses are a more complex combination, being composed of 4% glucose, 7% fructose, and 31% sucrose (Dionex 2003).

FT-IR data can show the ability of the biopolymer salt, once protonated to undergo cross linking with other biopolymer strands, to make larger and larger polymer units (Figure 2A). The reaction between amine moieties and protonated carboxylic acid groups to form a covalent carbon-nitrogen bond (Figure 2B) is observed by comparing biopolymer samples as the biopolymer salt and the same biopolymer salt after pH reduction.

Because gel permeation chromatography separates individual molecules based on their respective size relative to the swelling polymer that is used as a stationary phase, a correlation can be made between the retention time and the molecular weight of the material. Gel permeation chromatography on a size exclusion column was used to determine the distribution of molecular weight fractions of the biopolymer salt grown on corn syrup and molasses feedstocks (Figure 3). Each of the biopolymers demonstrated a different, and unique, molecular weight distribution of components. For example, the molasses-derived biopolymer exhibited components in both

the very small molecular weight range [approximately 150 dalton (Da)] and the much larger 800-Da range. Corn syrup-derived BP, on the other hand, showed a greater number of small molecular weight components (100-200 Da).

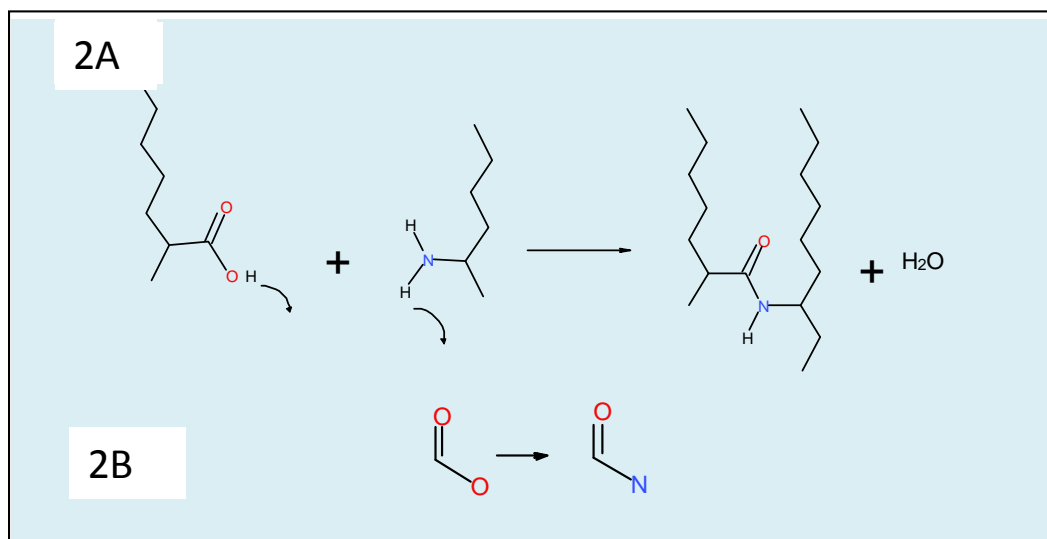


Figure 2. a) The polymerization reaction of the biopolymer, b) Highlighting the cross-linking reaction through the formation of covalently bonded amide linkages.

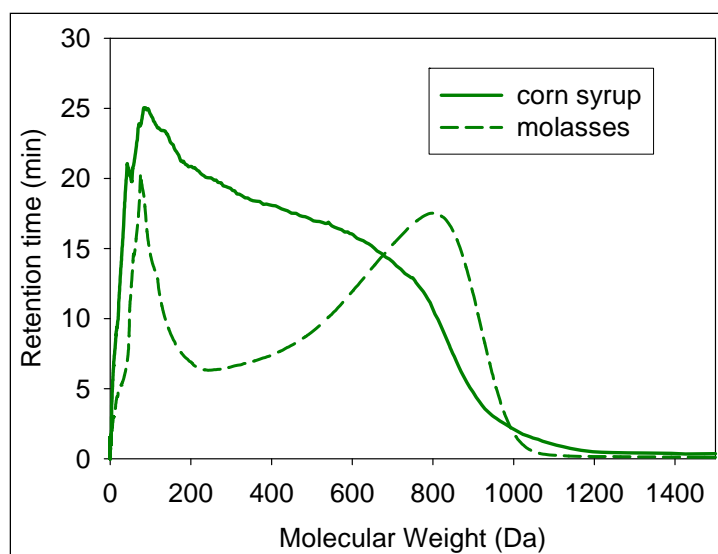


Figure 3. GPC evaluation of the of the *R. tropici* biopolymer salt grown using different carbon sources as feedstock.

Slope stability and erosion control

The ability to manage military installations in a sustainable, yet environmentally sound, manner that maximizes the time available for training and testing is a critical aspect of maintaining a fully operational and well trained

fighting force (JASON 2006). Eliminating off-site migration of heavy metals, reducing sediment transport off-range and reducing the impact of erosion on the range berm slopes and vehicular training areas are an integral part of managing small arms firing range (SAFR) facilities. From the standpoint of field operations personnel, the ability to provide non-eroding soils for operational areas is a critical aspect of the modern and effective fighting force.

Artificial petroleum-based soil strengthening and stabilizing additives are currently used for erosion control in areas where vegetation and geotextiles are inappropriate, such as SAFRs, and for dust control in areas where high winds and pressure pulses (natural or artificial) produce dust in quantities that reduce visibility (gun positions, rotary wing landing areas) (Newman et al. 2005, Tingle et al. 2007). Water and air erosion of soil is a concern for installation managers and requires extensive range maintenance to control, the cost of which has been known to equal \$7 billion (Ft. Bragg Surface Water Assessment Team 2009).

The synthetic, petroleum-based polymers currently used on training ranges for erosion control and dust abatement are based on an increasingly expensive and scarce natural resource. In addition, they are often difficult to transport and apply. Use of petroleum-based polymers also has an increasingly negative public perception due to their limited biodegradability and petrochemical nature. The ability to efficiently improve soil engineering properties is directly in-line with current military doctrine. Use of biopolymer stabilizing agents eliminates dependence on petroleum-based materials, leaves no lasting footprint, improves the cost-effectiveness and efficiency of live-fire training and maintains the ability of the US military to be good stewards of the nation's resources.

Metal migration

Heavy metal transport off ranges is a concern with both water and air erosion of soil and requires extensive range maintenance to control. Metals-contaminated dust is also potential health concern for troops. Munitions metals of concern include lead (Pb), antimony (Sb), chromium (Cr), copper (Cu), iron (Fe), and zinc (Zn). The presence of these metals in soil generates a number of environmental concerns associated with water quality and migration of the metals off-site.

Small arms ammunition is typically a Pb^{2+} alloy, primarily consisting of Pb^{2+} with smaller amounts of Sb, a hardening agent, and other metals, encased in a Cu and Zn shell casing/jacket (HQDA 1996; Weiss et al. 2005). Long-term use of SAFRs results in lead contamination from spent ammunition deposited within and adjacent to the targets. Metals occur in the form of discrete particles (intact bullets or shot, and fragments), metal salts (weathering products), and dissolved metal or metallic complexes adsorbed to the soil matrix. It has been documented that more than 96 % of the lead is present as intact or fragmented bullets or shot (ITRC 2003). Metals can then interact with soil in several ways:

- With the surface of particulate material in soils (adsorption),
- With specific contaminants (chemisorption),
- With inorganic and organic ligands (complexation),
- With inorganic soil constituents (e.g., carbonates, sulfates, hydroxides, sulfides) to form precipitates or ionic complexes.

Several investigators have demonstrated that lead ammunition exposed to the elements in surface soil will eventually oxidize to a soluble ionic form (Rooney et al. 2007, Prica et al. 2010).

Through the methods mentioned above, some metals become associated with suspended solids in runoff and/or leachate water. The suspended solid materials are entrained in the soil pore structure as colloidal, and sometimes cationic or anionic, metals. Studies at over 20 SAFRs have shown that the vast majority of lead leaving SAFRs is present as suspended solids in surface water runoff (Larson et al. 2005, Pennington et al. 2006). This allows for vertical migration through the soil structure towards water in the subsurface, such as a shallow water table. Eventually these materials settle out of the water over an area significantly larger than the initial area of interest where the munitions metals were deposited. Heavy metal-laden dust is also a potential health concern for troops. Eliminating off-site migration of heavy metals and reducing transport of contaminated sediment off-range are an integral part of managing SAFR facilities.

Best Management Practices (BMPs) have been suggested to control lead migration from active SAFRs (Fabian and Watts 2005, ITRC 2005, USEPA 2001). These include vegetative methods that control stormwater runoff, physical methods to manage stormwater, changes in berm design, the use of geosynthetic materials, physical separation techniques to remove large

bullet fragments from the soil, and soil amendments. Natural soil amendments involve the addition of lime, iron, or phosphate to the soil. These chemicals may mitigate the corrosion of lead in the soil, bind the lead ions in the soil pore water through adsorption, or promote the precipitation of lead ions and the formation of relatively insoluble lead species (Chen et al. 2007, Conesa et al. 2010, Davis et al. 2007, Fabian and Watts 2005, Martin et al. 2008).

Petroleum-based polymer additives that are available commercially, off-the-shelf to stabilize heavy metals in soils include SoilTac®, Gorilla-Snot® and DuraSoil®. These polymers all have a long, nanoparticle-based molecular structure that links and cross-links the soil particles. They are based on an increasingly expensive and scarce natural resource, they are often difficult to transport and apply, have limited biodegradability, and are reported to leach toxic metabolites into the soil (Weston et al. 2009). The use of petroleum-based polymers has an increasingly negative public perception; in addition, the possible environmental risk of adding nanoparticles to the soil remains under investigation (Glenn 2006).

Fugitive dust emissions

The National Ambient Air Quality Standards (NAAQS) are standards established by the U.S. Environmental Protection Agency (EPA) under authority of the Clean Air Act (42 U.S.C. 7401 et seq.) that apply to outdoor air throughout the country. The Clean Air Act was passed in 1963 and significantly amended in 1970 and 1990. Primary standards are designed to protect human health with an adequate margin of safety, including sensitive populations such as children, the elderly, and individuals suffering from respiratory disease. Secondary standards are designed to protect public welfare from any known or anticipated adverse effects of a pollutant (e.g. building facades, visibility, crops, and domestic animals).

NAAQS requires the EPA to set standards on six criteria air contaminants:

1. Ozone (O₃)
2. Particulate Matter (PM)
 - PM₁₀, coarse particles: 2.5 micrometers (µm) to 10 µm in size (although current implementation includes all particles 10 µm or less in the standard)
 - PM_{2.5}, fine particles: 2.5 µm in size or less

3. Carbon monoxide (CO)
4. Sulfur dioxide (SO₂)
5. Nitrogen oxides (NO_x)
6. Lead (Pb)

The standards (Table 1) are listed in Title 40 of the Code of Federal Regulations.

Table 1. USEPA Air Quality Standards for Particulate Matter

Pollutant	Type	Standard	Averaging time
PM10	Primary and secondary	150 µg/m ³	24-hr ^a
PM2.5	Primary and secondary	35 µg/m ³	24-hr ^b
PM2.5	Primary and secondary	15 µg/m ³	annual ^c

^a40 CFR 50.6

^b40 CFR 50.7

^c40 CFR 50.7

The EPA is currently deciding whether to further regulate coarse particulate matter (coarse PM) under the NAAQS of the Clean Air Act. EPA's Clean Air Scientific Advisory Committee's Particulate Matter Review Panel has been engaged in this issue to determine if scientific evidence suggests coarse PM is a health risk. The NAAQS include dust produced by driving on dirt roads among examples of dust that would be regulated under a coarse PM. EPA's proposals also call for regulating dust that is dominated by sources typically found in more urban areas, such as that produced during construction activities (Jan 17, 2010, Federal Register, "National Ambient Air Quality Standards for Particulate Matter" and Revisions to Ambient Air Monitoring Regulations"). These new regulations have the potential for high impact on testing and training ranges.

Controlling dust generation around military installations has been a concern for the Corps of Engineers since 1946. Controlling dust on military operational areas involves unique challenges. The U.S. Army requires an effective, efficient means of suppressing dust on airfields, helipads, cantonment areas, roads, and tank trails where the presence of dust was detrimental to military operations. When helicopters operate in dusty environments, their rotary blades and engines must be replaced after only one-third to one-half of their normal life due to surface erosion caused by airborne soil particles. Dust clouds around military installations from vehicular maneuvers provide the enemy with easily recognizable signatures

of strategic operations and impair visibility of both airborne and ground personnel (Grau 1993). The dust itself is a safety hazard for ground troops and, when mixed with particulate heavy metals from range ordnance, becomes an additional hazard.

Many of the polymer materials employed to mitigate the dust hazard are petroleum-based such as polyvinyl acetate, latexes, and emulsions, the hazards of which have been discussed above. The objective of this portion of the biopolymer research was to evaluate the ability of the biopolymer to reduce production of fugitive dust.

2 Experimental Design

Objectives

This biopolymer investigation involved three separate studies evaluating its performance related to slope stability, metal migration, and fugitive dust emissions.

Slope stability and erosion control

The objectives of this first study were to provide a performance evaluation of the biopolymer in the areas of:

- Slope stability on earthen berms, and
- Reduction of soil erosion and surface water transport of sediment contributing to elevated suspended solids.

Metal migration

The objective of this study was to provide a performance evaluation of the ability of biopolymer, derived from three different carbon source feed stocks to stabilize heavy metals in soil.

Fugitive dust emissions

The objective of the third study was to ascertain the ability of the biopolymer to reduce production of fugitive dust from a dust-producing soil across a range of relative humidity conditions.

Experimental design

Slope stability and erosion control

Biopolymer soil amendment was evaluated for its contribution to both slope stability and surface soil durability. Simulated berms were constructed at the angle of repose characteristic of earthen berms in slope stability boxes. Prior to construction, experimental soils were amended with biopolymer at dosing rates of 0%, 0.2%, and 0.5% biopolymer (w:w) and compared to an untreated control of the same soil type. The biopolymer was produced using a molasses-based feedstock. Artificial rainfall was added to the berms weekly in amounts to simulate both yearly and extended rainfall and

weathering of a berm. One weekly rain event is equal to 4.33 weeks of weathering time, approximately one month. Soil mass lost was empirically measured for each slope. Leachate and runoff water were collected weekly for 12 weeks (one year of simulated weathering) and analyzed for total suspended solids (TSS). The soil types used in the experiments were Silty Sand and Silt, classified SM and S, respectively, according to the Unified Soil Classification System (ASTM 2011). Static mesoscale rainfall lysimeters were used to evaluate the ability of the biopolymer to reduce soil erosion and the transport of sediment in both surface runoff water and leachate.

Metal migration

Static mesoscale rainfall lysimeters were also used to evaluate the ability of the biopolymer to reduce heavy metal transport in surface runoff water and leachate. The Silty Clay (SC) soil in the static lysimeter was amended with 0.2% biopolymer grown from a mixed carbon source feedstock. The control was unamended soil. Each lysimeter received weekly rainfall; the leachate and runoff water samples were collected 24 hr following each rainfall event. The leachate and runoff water was analyzed for metals and TSS.

Dynamic lysimeters were used to evaluate the ability of the biopolymer to reduce heavy metal transport in surface water runoff and leachate following live-fire exercises. The soil used in these live-fire lysimeters (LFLs) was a Sandy Silt with gravel (ML) amended with 0.2% (w:w) biopolymer grown on either corn syrup, molasses, or sorghum feed stock. Two controls were used: an unamended soil that did not receive live-fire and an unamended soil that received live-fire weekly. Each lysimeter received weekly rainfall and the leachate and runoff water samples were collected 24 hr following each rainfall event. The leachate and runoff water was analyzed for metals and TSS.

Fugitive dust emissions

Dust suppression was measured at three biopolymer loading rates in a Silty Sand (SM) soil type. The biopolymer was grown using a molasses-based feedstock as the carbon source. The test method developed for this evaluation was designed to provide a mechanism for rapidly screening multiple chemicals in various application scenarios in order to make inferences about performance. The testing protocol was a method developed by Rushing and Newman (2010), which was designed specifically for products intended for preventing dust generated by wind erosion.

3 Materials and Methods

Materials

Experimental soils

The four experimental soil types used in the treatability studies—Silty Sand, Sandy Silt, Silt (Loess), and Silty Clay—were selected because they are prone to wind and water erosion thus presenting possible worst-case scenarios.

Biopolymer amendment

The biopolymer evaluated in the slope stability boxes and for reduction of fugitive dust was produced using molasses as a carbon source for bacterial growth.

Three types of biopolymer were tested for their effectiveness at reducing migration of heavy metals in soil; they were produced using three carbon sources as feedstock: sorghum, molasses, and corn syrup.

Slope stability boxes

The slope stability boxes to evaluate berm longevity on SAFRs were constructed from 1.905-cm thick, high-density polyethylene. The inside dimensions of each box was 0.7874 m (2 ft, 7 in.) long by 0.7874 m (2 ft, 7 in.) wide by 0.6096 m (2 ft) in height. A delivery system for the artificial rain is used with the slope stability boxes and the rainfall lysimeters to simulate yearly rainfall and weathering. Both study systems were designed to collect the leachate percolating through the soil and the runoff from the soil surface. Leachate and sediment flowing with the water were collected in polyethylene pans (Figure 4). Two soil types (SM and S) were examined in the slope stability boxes at three biopolymer loading rates: 0% (control), 0.2% w:w, and 0.5% w:w.

Mesoscale rainfall lysimeters

Standard mesoscale rainfall lysimeters (Figure 5) were used to study erosion on bermed SAFRs and heavy metal migration with suspended solids from unbermed ranges. Assembly and use of the rainfall lysimeters

are described in Larson et al. (2005). Both studies used Silty Clay (CL) soil type. The experimental soil was amended with 0.2% biopolymer (w:w) and compared to its untreated control after each rainfall event. The CL soil as used was an aged soil contaminated with munitions residues.



Figure 4. Slope stability boxes with unamended control cells on left and 0.2% biopolymer cells on right. The soil types in each pair are Silty Sand on left and Silt on right. Note the clarity of the leachate water from the biopolymer-amended soils on the right.

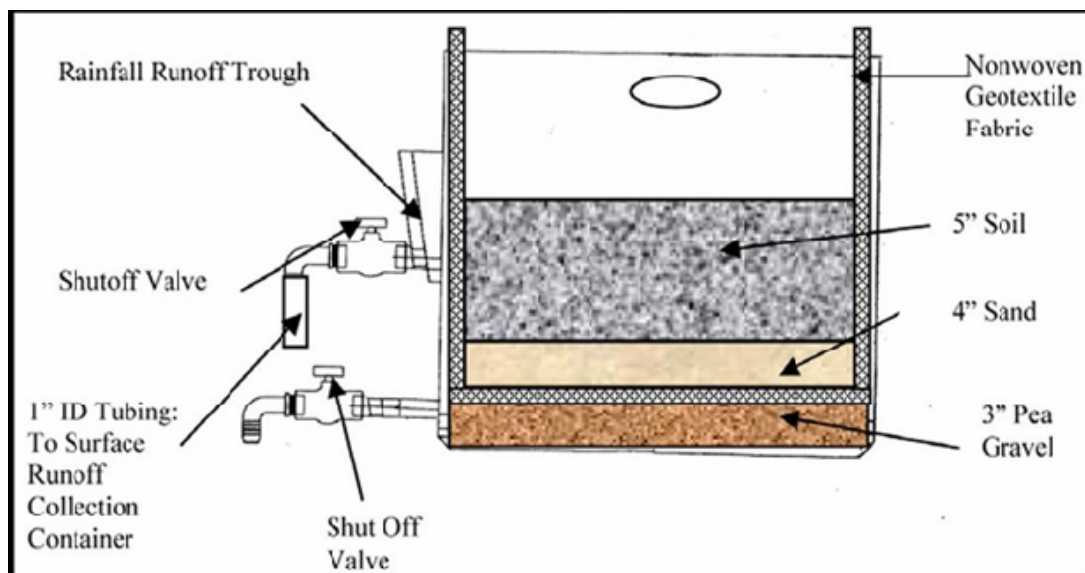


Figure 5. Mesoscale rainfall lysimeter.

Live-fire lysimeters (LFL)

The LFL test system differs from the static mesoscale lysimeters in that the soil loaded into the lysimeter is augmented by live-fire ammunition. The LFL accounts for active bullet loading into a berm or impact on unbermed soil; it reflects the dynamic effects of the bullet loading on the total suspended solids. The LFL also accounts for the effects of bullet-to-bullet impacts and the general effects of the soil disturbance in the impact area. Figure 6 shows an example of a LFL cell, which is surrounded by SACON® blocks to prevent bullet ricochet. The top is covered with plywood to prevent soil ejecta from contaminating adjacent cells. For this treatability study, the toe area of the berm was extended outward to simulate target impact areas. The toe area had its own leachate collection system (Lower Leachate, LL) distinct from the berm collection system (Upper Leachate, UL). This system is illustrated in Figure 7, showing a LFL unfilled and filled with the experimental soil.

The soil used in the live-fire lysimeters is classified as Sandy Silt with gravel (6.6% gravel, 42.7% sand, 50.7% fines). Three types of biopolymer were tested for their effectiveness at stabilization of heavy metals in soil. The biopolymer was produced using three different carbon sources: sorghum, molasses, and corn syrup (Table 2).



Figure 6. A live-fire lysimeter cell.

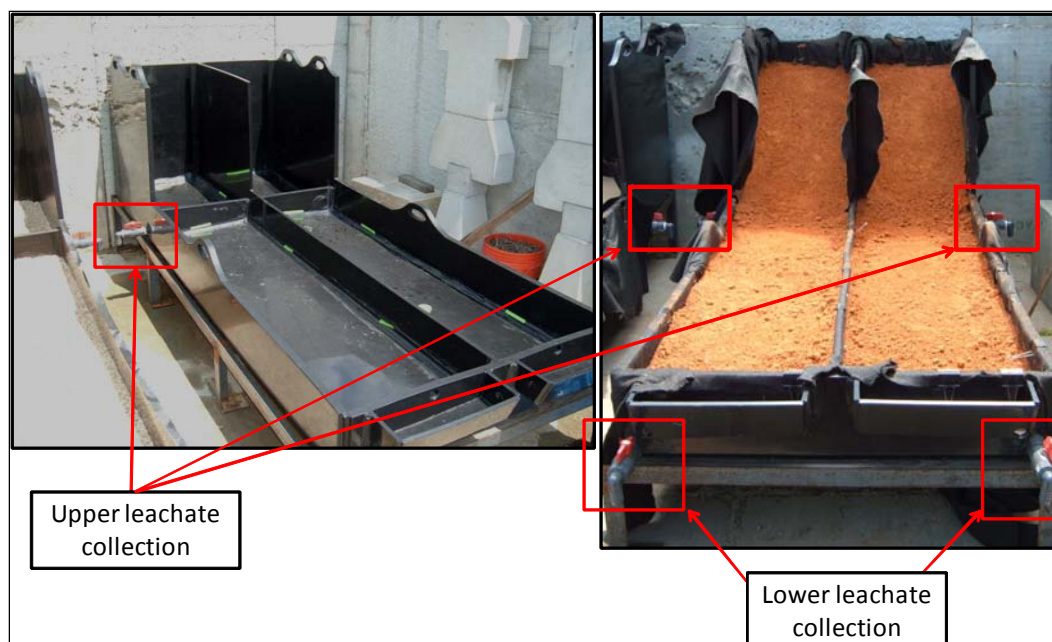


Figure 7. Photographs illustrating the upper and lower leachate and surface water collection systems in the extended toe LFL.

Table 2. Lysimeter cell and amendment.

Lysimeter	Amendment
1	Control – no amendment, no firing
2	Control – no amendment
3	Sorghum BP ^a
4	Molasses BP
5	Corn syrup BP

^aBP=biopolymer

Dust palliative spray device

A spray device was designed and fabricated that would give uniform soil application that was consistent between samples. Spray nozzles, flow rates, and application velocity were used to achieve volumetric and geometric spray profiles equivalent to field application equipment. The liquid dust palliative was diluted (if stated) and poured into an aluminum canister. The canister was equipped with a ball valve and a plastic, wide fan spray nozzle on the bottom. The spray nozzle used is the same as that found on many commercial dust palliative sprayers. The top of the canister had a port for attaching an air hose to pressurize the canister and achieve the necessary fan width from the spray nozzle. This system required calibration because higher-viscosity liquids required greater pressures to obtain equal flow

rates. The canister was mounted onto a carriage attached to a transfer mechanism. Uniform displacement rates were achieved using a rack and pinion system powered by a variable-speed DC motor. Travel speeds were adjusted using a rheostat and dial gauge to obtain calibration for achieving the desired application rates based on both speed and volumetric output. Details of the device are supplied in Rushing and Newman (2010).

Methods

Slope stability boxes

A rainfall event was conducted weekly over each slope stability box for 16 weeks, which simulated weathering time of approximately 1.25 years based on average rainfall of 47-51 in. per yr for the Eastern United States. To assess soil movement and erosion potential, the slope angle of each simulated berm was measured spatially each week. In addition, the increase in the amount of soil deposited in the range floor area of the slope stability box (constituting lost soil mass in the simulated berm) was recorded. Leachate and runoff water samples were collected 24 hr following each rain event. After recording their volumes, the samples were analyzed for TSS.

Mesoscale rainfall lysimeters

Using mesoscale laboratory rainfall lysimeters, rainfall was conducted weekly for 12 weeks unless otherwise stated. Leachate and runoff water samples were collected 24 hr following each rain event. The volume of each was measured and recorded and the samples were split for analysis of TSS and metals.

Live-fire lysimeter

Firing specifications

The two M16A2 weapons used in this test (serial numbers 7435556 and 7434589) had specifications as provided in Table 3. The cadence of test firing was 2-3 rounds per minute. The weapons were mounted in a Lone Star Field Products VR555B SPEC-REST with bench base and fired from bench rest position. After 600 rounds, the guns were fully disassembled, cleaned, and lubricated before being placed back into operation.

The berms were fired into weekly for 10 weeks using 150 M-16 rounds of 5.56-mm bullets per event, thus a total of 1,500 bullets were fired into each cell over the course of the entire study. When test formulations of the

biopolymers formed a surface “crust”, the top and the toe area of the lysimeter were covered with plywood to prevent soil spattering into adjacent lysimeters.

Table 3. Weapon specifications for the live-fire lysimeter study.

Military Designation	Barrel Length	Barrel	Handguard Type	Buttstock Type	Muzzle Device	Trigger Pack
M16A2	20 in. (508 mm)	A2 profile (1:7 twist)	Full-length ribbed	Fixed A2	M16A2-style birdcage flash suppressor	Safe-Semi-Burst

Weathering and sampling

Rainfalls were conducted following the firing events. The experiment simulated one year of annual rainfall in an Eastern US site (47-51 in) in 10 weeks. The runoff water and leachate were collected weekly and analyzed for TSS and heavy metals.

Fugitive dust emissions

Test specimens were prepared in 15 cm (6 in.) by 15 cm (6 in.) square molds that were 5 cm (2 in.) deep. The soil used for each test was classified as a Silty Sand (SM). The material was processed prior to use by oven drying to remove moisture.

Using the sprayer system described above, each sample received a single application of biopolymer or distilled water (control) of 1.125 L/m² (0.25 gal/yd²). Samples were placed under infrared lamps and adjusted to a height that would produce surface temperatures of 49 °C (120 °F) for curing. Samples were removed after 48 hr of curing time. The sample listed as 0% humidity was tested immediately after removal. The other samples were placed in an environmental chamber at 25 °C (77 °F) and either 40% or 95% humidity until a constant weight was achieved.

Samples were tested in a chamber designed to simulate wind velocities encountered near aircraft. The testing chamber measured 1.2 m (4 ft) long, 0.3 m (1 ft) wide, and 0.6 m (2 ft) tall. It was sealed from external air to prevent dust from escaping during testing. Air velocities of 241 km/hr (150 mi/hr) were generated by an electric fan motor and transmitted through a 7.5-cm (3-in.) PVC pipe to a rectangular aperture 11.4 cm (4.5 in.) wide and 1.25 cm (0.5 in.) tall. Average maximum air velocities were measured using a Kurz model 2442 anemometer. A return air duct

circulated air from the testing chamber to the electric fan to equilibrate pressure. Air blasts were initiated 2.54 cm (1 in.) above the sample at an angle 20 degrees from horizontal and lasted for 30 seconds. Additionally, during the air impingement test, 300 grams (g) of Ottawa sand (US sieve size #20-30) was injected into the air stream. The sand injection increases surface scour and is intended to replicate actual conditions as suspended dust particles impart additional abrasion to the ground surface. Ottawa sand provides a uniform, consistent material that does not impact the optical sensor measurements.

Sample analysis

A Hach DR/200 spectrophotometer read at 810 nm was used to analyze samples for TSS.

Total (digested) metals were determined on aqueous samples (leachates and runoff waters) after digestion according to EPA SW-846 Method 3015 (1999). Soluble metals (<0.45 micron) were determined after sample filtration [Method 3010, American Public Health Association (APHA) 1998]. Analysis was performed using Inductively-Coupled Plasma (ICP) on either a Perkins Elmer Optima 3000 (SW-846 Method 6010) or a Perkins Elmer Sciex 6000 (SW-846 Method 6020). While Pb has historically been the heavy metal of greatest interest when discussing transport of munitions metals off-range, all munitions-derived metals were quantified for both soluble and total concentrations: Pb, Cr, Cu, nickel (Ni), Zn, Fe, manganese (Mn), molybdenum (Mo), vanadium (V), Sb, and arsenic (As).

4 Results and Discussion

Slope stability and erosion control

Soil loss

Following a series of 12 weekly rain events in the slope stability boxes (equivalent to one year of rainfall), untreated Silty Sand soil had lost 40.0 kg of soil mass (69% of the total soil mass). Untreated Loess (Silt) soil lost 32.0 kg, 66% of the total mass. In contrast, the same soils when treated with 0.2% biopolymer (w:w), lost 8.0 kg (approximately 17% of the total mass, Silty Sand) and 1.0 kg (approximately 1% of the total mass, Loess (Silt) soil). The mass lost from each “berm” is shown in Figure 8 for each soil type and each biopolymer loading rate. The untreated soils each lost the greatest soil mass, followed by the soils that were treated with 0.2% biopolymer (w:w). The soils treated with 0.5% biopolymer (w:w) each maintained a stable mass throughout a year of simulated weathering (i.e. 12 weekly rain events).

Rain events were continued for an additional 7 weeks (19 weeks total) to observe retention of the biopolymer soil binding characteristics. The biopolymer-treated soil continued to demonstrate surface durability and resistance to erosion after 19 rain events, the equivalent of 1.7 years of weathering. This is visible from examination of the soil surface (Figure 9), where the sub-surface gravel was exposed by weathering in the untreated soil.

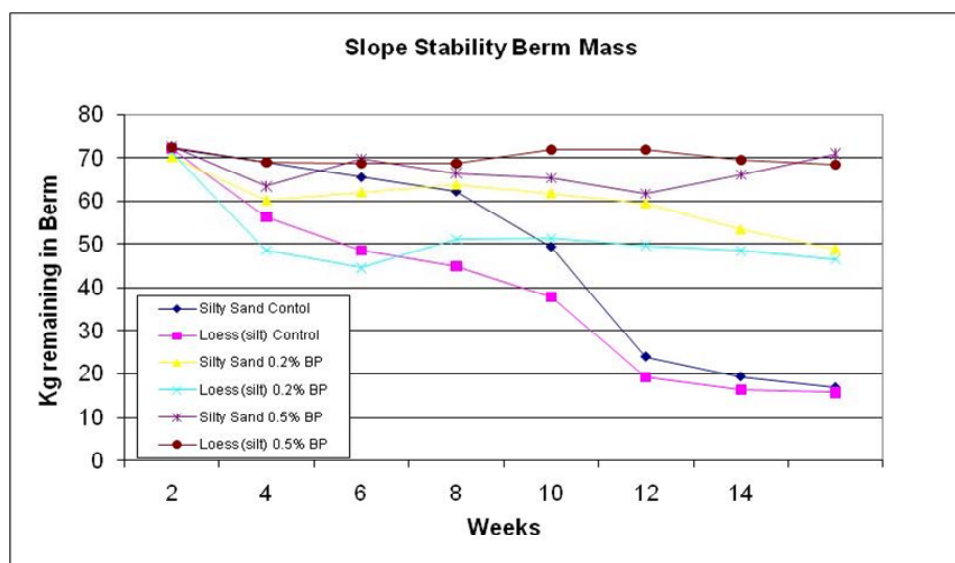


Figure 8. Mass lost by soil type and biopolymer loading rate.



Figure 9. Illustration of the surface durability and resistance to erosion of biopolymer amended soil over the untreated control.

Sediment load in runoff

Sediment loads were measured in runoff water and leachate from treated and untreated Silty Clay soil during the slope stability experiments (Figure 10). Biopolymer amendment resulted in a 78% decrease in TSS in the runoff water. The reduction in TSS in the leachates was approximately 50%. Particle size analysis of treated and untreated soil demonstrated that the percentage of material in the >0.3-mm particle-size fraction increased by 22% in the biopolymer-treated soil. The biopolymer, performing its natural function as a soil binder, was very effective in this soil type at reducing the loss of sediment in runoff water. While a 50% reduction of TSS in the leachate is significant, the different effect of the biopolymer between the leachate and the runoff water can be attributed to the fact that the biopolymer is applied to the surface 6 in of soil and the leachate water has greater contact time with unamended soil. Repeated application of the biopolymer may result in a deeper reactive zone further reducing the leachate TSS.

Leachate and runoff water were also collected from the LFL system for 16 rain events and analyzed for TSS (Figure 11). At the completion of this portion of the study (a simulated 1.25 yr weathering), the amount of TSS in the runoff water from the BP-treated soil was reduced by 40 % relative to the control. However, TSS concentrations in the runoff water began to increase after the equivalent of 10 months of weathering (12 rain events).

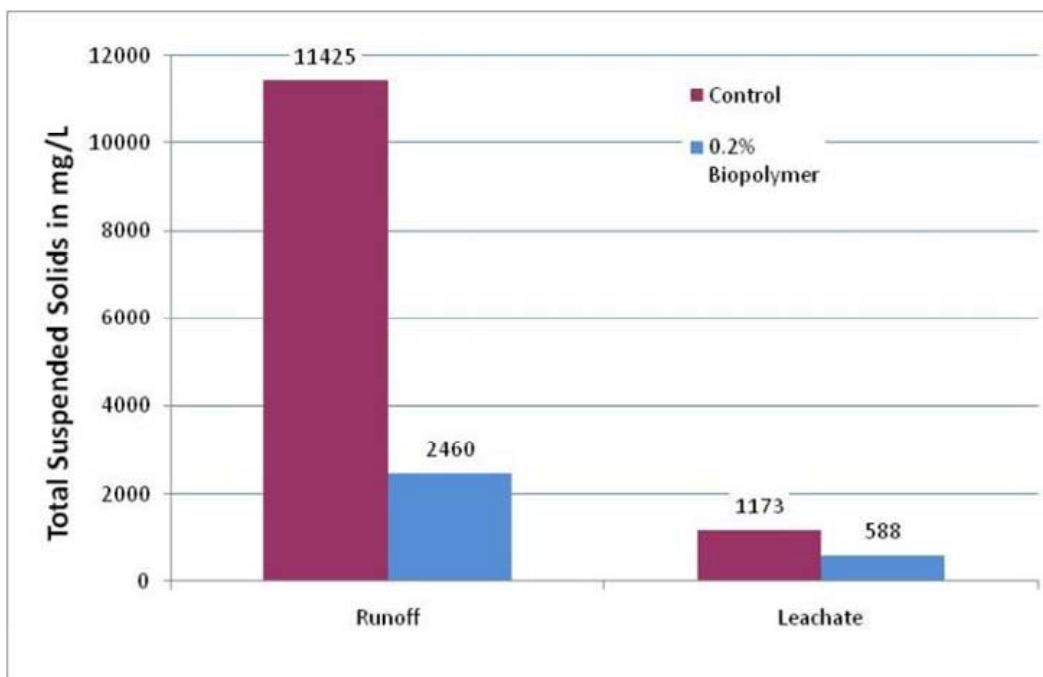


Figure 10. Comparison of TSS in runoff water and leachate from control and biopolymer-amended Silty Clay soil during the slope stability studies as run in the static mesoscale lysimeter systems.

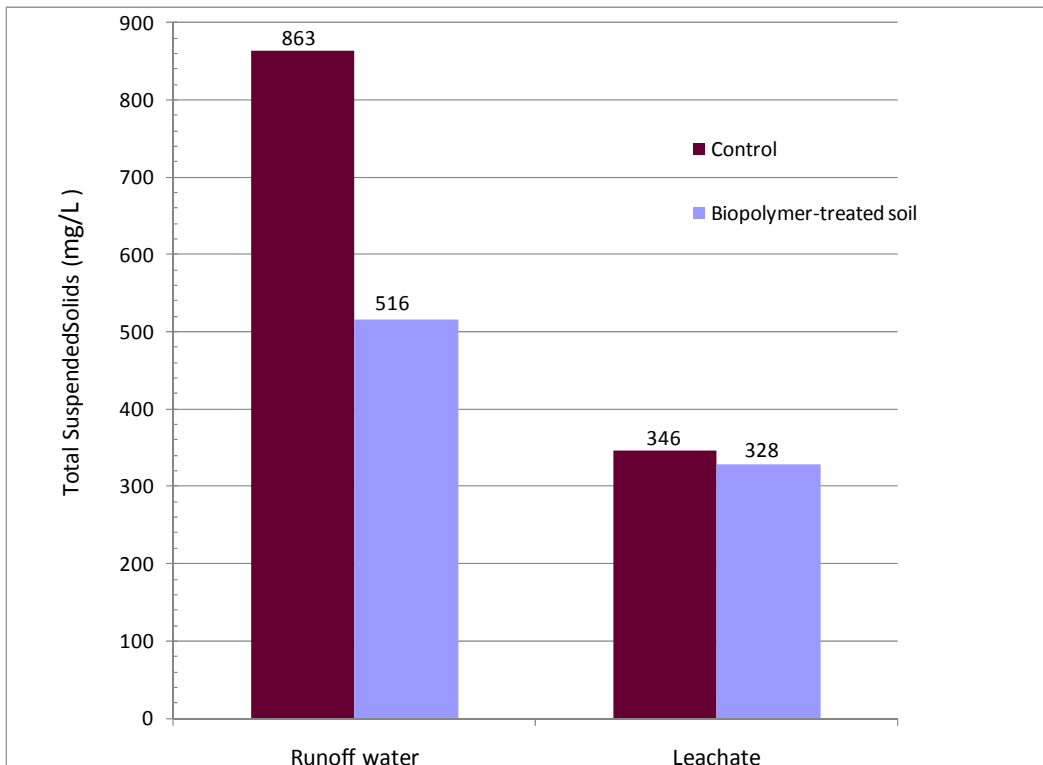


Figure 11. Total suspended solids in runoff water and leachate from untreated and biopolymer-amended metals-contaminated soil in the live fire lysimeter after 1.25 yr simulated weathering.

At this point, the reduction from the untreated control by the biopolymer treated soil was 53%. This would indicate that biopolymer should be re-applied to the soil every 10 to 12 months. The effect of the biopolymer is not as great on leachate TSS as only the surface 6 in. of soil were treated with the biopolymer.

As seen by the decrease in TSS with biopolymer soil amendment in the mesoscale and live-fire lysimeters, when the biopolymer is added to the soil and wetted, either by rainfall or normal soil moisture, the soil acts as a buffer, neutralizing the ionic character of the biopolymer salt. The biopolymer can then begin reacting with itself and the constituents of the soil matrix. The reactive, cross-linked biopolymer has a larger molecular weight and a reduced water affinity. It links together the individual soil particles within the biopolymer matrix. The individual soil particles of the amended soil have greatly reduced mobility, significantly reduced hydraulic conductivity, and compressive strength equal to that produced by synthetic polymer amendments. It is this change in the physical form of the soil, on a particle level, that results in increased soil strength and decreased soil erosion.

Heavy metals in leachate and runoff water

Heavy metal transport was studied using the mesoscale rainfall lysimeters, a static system, and in the larger, dynamic, live-fire lysimeters. Rain events were conducted at weekly intervals. The static lysimeters were run for 12 weeks (1 year simulated weathering). The LFL controls were run for 20 rain events for a simulated 1.7 years of weathering. Various biopolymer formulations and application methods were evaluated for a minimum of 4 rain events (approx. 4 months simulated weathering time). If the formulation/application method did not meet performance objectives it was discontinued at that time.

The mass of total Pb (particulate plus dissolved forms) detected in the leachate and runoff water from control (untreated) and biopolymer-amended soil after 16 weeks (1.25 years of simulated weathering) is shown in Figure 12 for the static lysimeter system. The data shows a 97% reduction in total Pb in the runoff water from biopolymer-amended soil; 94% reduction in leachate from the same soil.

The values for dissolved Pb (data not shown) were either below or close to the method detection limits (0.5 mg/kg) for both treated and untreated soil.

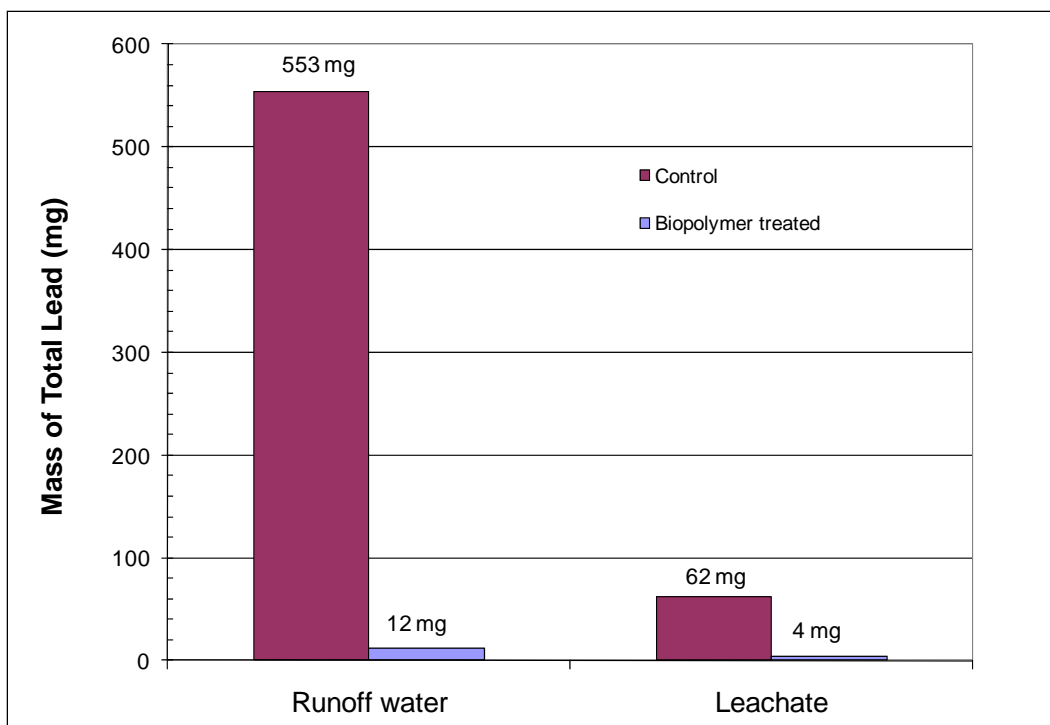


Figure 12. Mass of total lead in runoff water and leachate from untreated and biopolymer-amended metals-contaminated soil after 1.25 year of simulated weathering using the static mesoscale rainfall lysimeter.

Earlier research has shown that dissolved heavy metals are transported in surface water and leachate by sorption to soil particulates and colloids (Larson et al. 2005). For heavy metals to become stabilized, it is important that the biopolymer cross-links around the adsorbed metal and soil particle, which reduces the mobility of the soil particle in water and the transport of the heavy metal. Because the biopolymer was applied only to the surface 6 in of soil, runoff water was exposed to the biopolymer for a longer time than was the leachate. Biopolymer added to the soil of the lysimeters was successful at decreasing the concentration of lead, particularly in surface water runoff.

The LFL experiment was modified after 4 rain events (equivalent of 4.3 months) due to surface “crust” formation that interfered with firing and water adsorption. The surface application method was modified by covering the treated soil with a layer of untreated soil. This modification prevented the formation of the soil “crust”. Table 4 presents results of dissolved Pb transport in the LFL after the modified application procedure for both the upper and lower leachate from the fired control and the three carbon source biopolymer-amended soils. The soil amended with the molasses-derived biopolymer had the lowest mass of dissolved Pb in both the upper and lower

leachate. It is notable that the soluble Pb in the lower and upper leachate in the sorghum and corn syrup biopolymer-amended plots were higher than the control (no amendment) and the molasses-derived biopolymer plot.

Table 4. The mass of dissolved lead (Pb) in the upper and lower leachate from the control (fired) soil and biopolymer-amended lysimeters following 4 rain events (equivalent to 4.3 months weathering).

Soil treatment	Mass of Dissolved Pb (mg)	
	Upper Leachate	Lower Leachate
Control (fired)	0.03	6.91
Sorghum syrup	0.97	23.33
Molasses	0.19	4.09
Corn syrup	1.34	19.65

Metal ions can form complexes with natural organic matter (NOM), which can impact metal mobility through increased solubility and decreased sorption to soils. The biopolymer in this engineered system is an EPS that constitutes a major component of NOM in natural systems. The three forms of EPS biopolymer present vary in the nature of formation of organo-Pb complexes based on the composition of the EPS functional groups (e.g., carboxylic, amine, hydroxyl). Molasses produced more carboxylic acid groups than the corn syrup-based material and was composed of high molecular weight EPS units (as high as 800 KDa). Corn syrup-derived biopolymer, on the other hand, showed a greater number of small molecular weight components (100-200 KDa). The presence of smaller molecules capable of complexing with lead and migrating in water in the corn syrup and sorghum-based biopolymers is consistent with the data in Table 4.

The mass of total lead in the upper and lower leachate from the control and molasses-derived biopolymer-amended soil are shown in Figures 13 and 14, respectively. The molasses-based biopolymer was effective at reducing lead in the upper leachate for the first three weeks, then lead started increasing in the fourth week. Not shown are the results of the corn syrup- and sorghum syrup-based biopolymers, which were significantly worse and less consistent at immobilizing lead.

The mass of total Pb in the lower leachate from soil treated with the molasses-derived biopolymer began to increase after the second rain event (equivalent elapsed time of 2 months). This contrasts with the results from

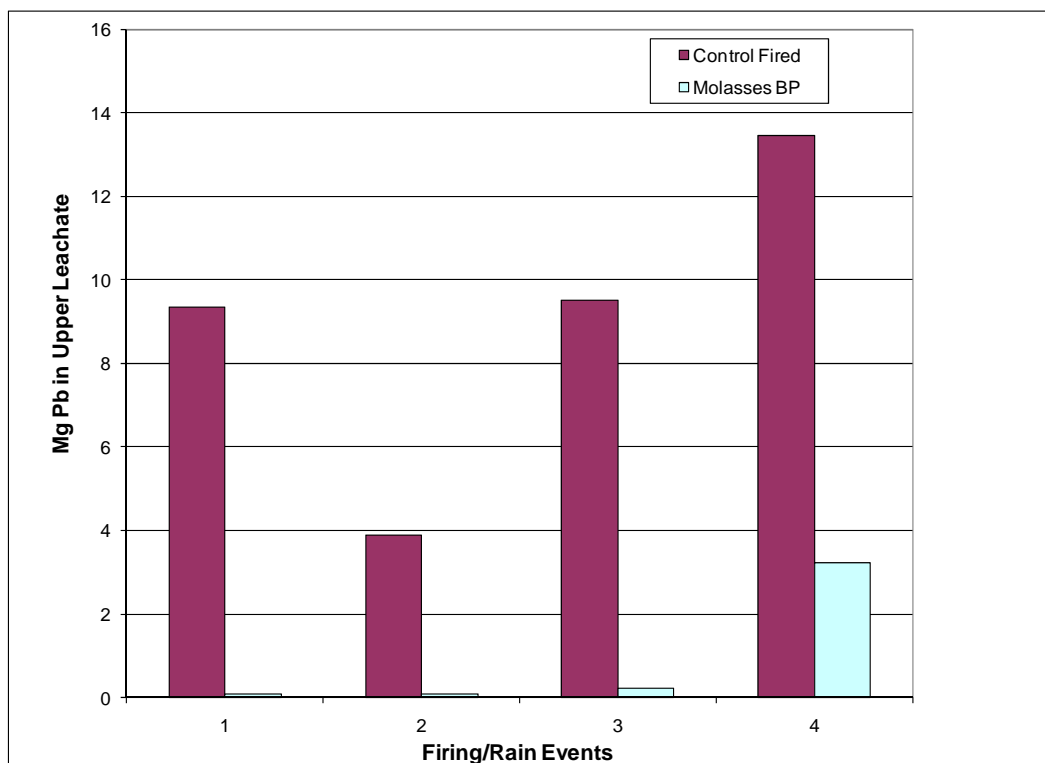


Figure 13. Mass of total lead (Pb) in the upper leachate from soil amended with biopolymer from molasses-derived carbon feedstocks.

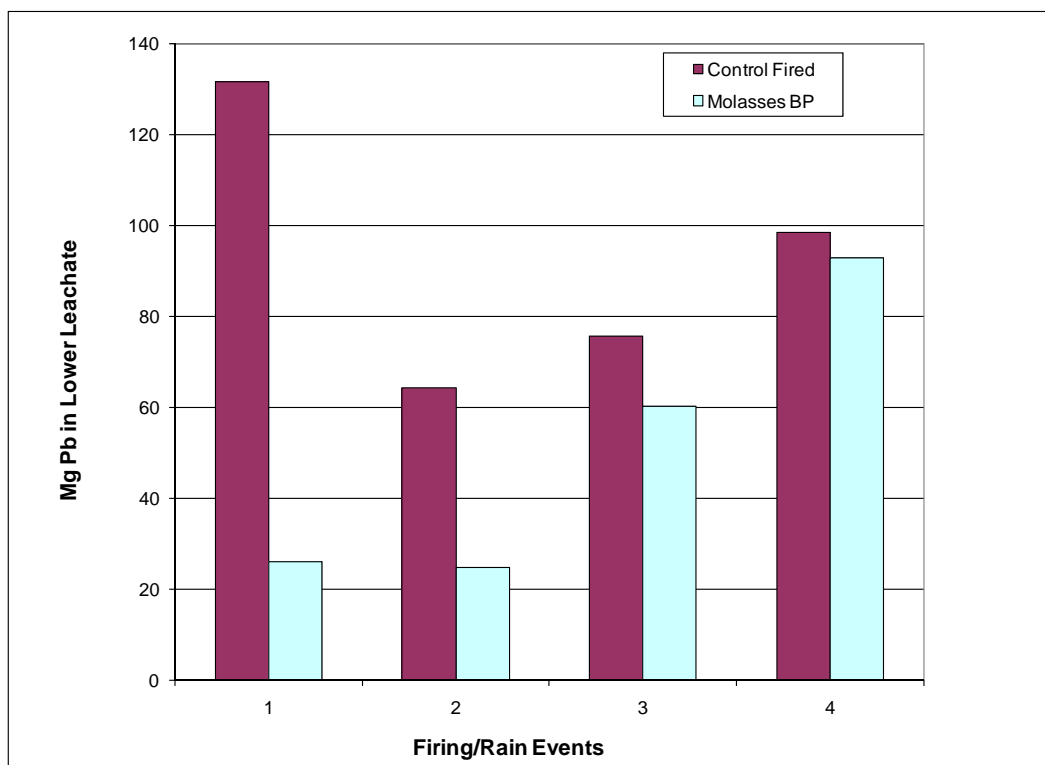


Figure 14. Mass of total lead (Pb) in the lower leachate from soil amended with biopolymer from the molasses-derived feedstock.

the static (no live firing) lysimeter study (Figure 12). The differences can be accounted for, in part, by the weekly disturbance of the bond between the biopolymer and the soil by the bullet impacts. Another factor is the contact time of the leachate with unamended soil in the lysimeter, which is greatest in the lower leachate. With continued regular application of the biopolymer a “reactive” zone should be created at greater depth in the soil. Based on the current data, however, re-application would be recommended on a quarterly basis as part of regular range impact area maintenance.

Fugitive dust emissions

Figure 15 shows the mass loss from untreated Silty Sand soil and from the same soil treated with three biopolymer doses at three relative humidity levels.

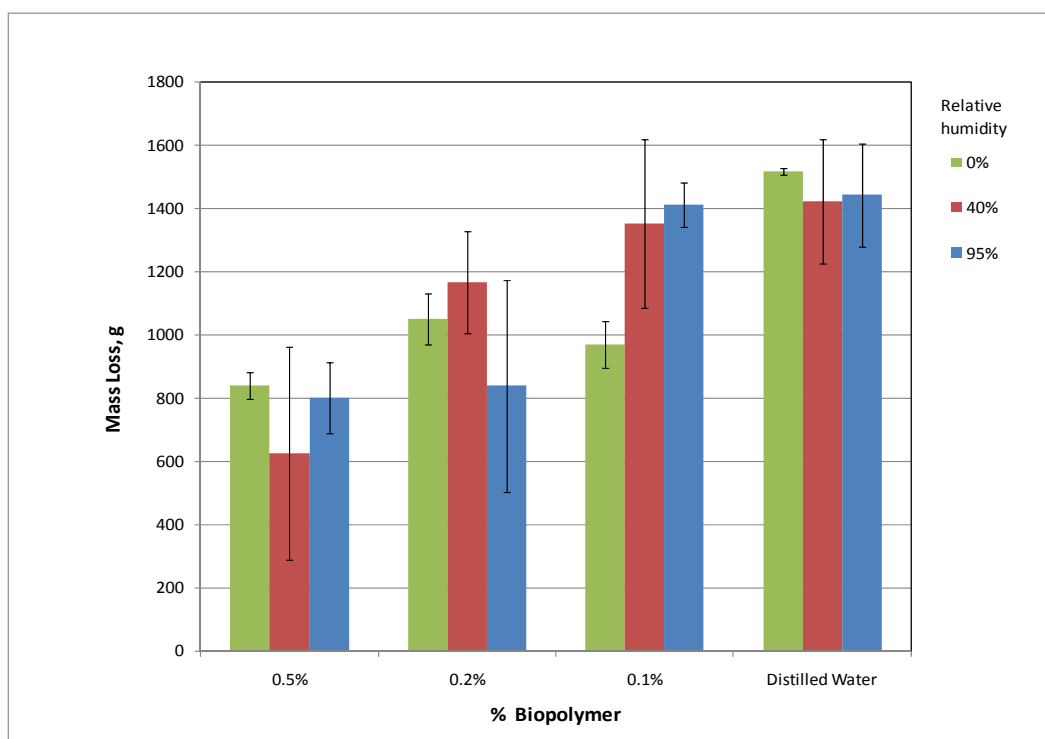


Figure 15. Comparison of mass loss from Silty Sand soil treated with biopolymer at three loading rates and three relative humidities.

Within the replicate studies, there appears to be no statistically significant variation in dust production with varied relative humidity when using the Rushing/Newman dust measurement system. Biopolymer added to the soil at 0.5% (w:w) loading rate reduced dust production compared to the control at all relative humidities, indicating it should perform well in both arid and tropical environments. A mass loading of 0.5% requires a range of

product amount per acre depending on the depth of soil treated. Table 5 lists the mass of biopolymer required to achieve reduced fugitive dust from this soil type for three application depths.

Table 5. Biopolymer mass required for a 0.5% application rate for three application depths.

Treatment depth (in.)	BP Application Rate	
	g/yd ²	kg/acre
1	140	17.5
2	280	35
3	420	52.5

Depending on the depth of soil treated, low masses of biopolymer amendment could be used to reduce dust emissions from large areas. The natural, biogenic nature of the biopolymer is expected to greatly reduce environmental impact associated with the use of biopolymer as a dust control technology. Additionally the tendency of biopolymer-amended soils to promote vegetative cover might be expected to further reduce mass loss at the periphery of dust producing areas where plants can survive and stabilize topsoil.

5 Conclusions

Slope stability and erosion control

The objectives of this project were to provide a performance evaluation of the biopolymer in the areas of:

- Slope stability on earthen berms, and
- Reduction of soil erosion and surface water transport of sediment contributing to elevated suspended solids.

In response to these objectives, the treatability study on the use of biopolymer to improve slope stability on bermed ranges and reduce loss of sediment in surface water runoff showed that the biopolymer amendment:

- Effectively maintained the slope stability of a simulated berm,
- Reduced transport of soil particulates in surface runoff, and
- Performed effectively in soils with a high concentration of fines.

This study of sediment transport demonstrated that the biopolymer soil amendment was able to significantly reduce surface water erosion and particulate transport in leachate.

Metal migration

The ability to efficiently improve soil engineering properties is directly in-line with current military doctrine. The objective of this project was to provide a performance evaluation of the biopolymer in the area of heavy metal stabilization using:

- Static rainfall lysimeters, and
- Live-fire lysimeters.

Treatability studies mixing *R. tropici* biopolymer salt with firing range soils that were contaminated with munitions constituents (e.g. metals such as lead, antimony, etc.) produced the following results:

- In static lysimeters, Pb transport from biopolymer-amended soil was reduced by >97% in both leachate and surface water relative to the unamended control.
- In the live-fire lysimeters, surface application of biopolymer resulted in a soil “crust” that produced scatter of soil upon impact. Crust formation was decreased by covering the surface biopolymer with a thin layer of untreated soil.
- The molasses-derived biopolymer produced the greatest decrease in transport of Pb and TSS.
- The biopolymer modifications and the engineering changes to the berm structure showed that biopolymer was able to reduce TSS and Pb transport in surface water and leachate under live-fire conditions.

Fugitive dust emissions

The objective of this portion of the biopolymer research was to ascertain the ability of the biopolymer to reduce production of fugitive dust. The treatability study demonstrated that the biopolymer soil additive has the potential to suppress dust on airfields, helipads, cantonment areas, roads, and tank trails where the presence of dust is detrimental to military operations. It also has the potential to suppress dust from construction activities. Biopolymer added to the soil at 0.5% (w:w) loading rate reduced dust production compared to the control at all relative humidities, indicating it should perform well in both arid and tropical environments.

A low-cost, biopolymer-based (i.e. non-petroleum-based) amendment for range soil that reduces the propensity of the munitions metals to mobilize in surface waters and/or leach to groundwater (especially shallow water tables or during large rainfall events) would greatly reduce the potential environmental risks associated with SAFRs, including private and public sport shooting ranges. Use of biopolymer stabilizing agents eliminates dependence on petroleum-based materials, leaves no lasting footprint, improves the cost-effectiveness and efficiency of live-fire training and maintains the ability of the US military to be good stewards of the nation's resources. Biopolymers have been shown to be effective alternatives for the petrochemical-based polymer soil additives currently in use.

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1. REPORT DATE (DD-MM-YYYY) August 2012		2. REPORT TYPE Final report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Biopolymers as an Alternative to Petroleum-Based Polymers for Soil Modification; ESTCP ER-0920: Treatability Studies				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Steven L. Larson, John K. Newman, Christopher S. Griggs, Milton Beverly, and Catherine C. Nestler				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Research and Development Center Environmental Laboratory 3909 Halls Ferry Rd., Vicksburg, MS 39180-6199; Geotechnical and Structures Laboratory 3909 Halls Ferry Rd., Vicksburg, MS 39180-6199; Environmental Research and Development, Inc. 1015 Meadow Street, Vicksburg, Ms. 39180; Applied Research Associates, Inc., Southern Division 119 Monument Place, Vicksburg, MS 39180				8. PERFORMING ORGANIZATION REPORT NUMBER ERDC TR-12-8	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Corps of Engineers Washington, DC 20314-1000				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <i>Rhizobium tropici</i> , a catalogued symbiotic nodulator of leguminous plants, is also known for its production of a gel-like extracellular polymeric substance (EPS). The natural functions of the biopolymer in the rhizosphere include surface adhesion, self-adhesion of cells into biofilms, formation of protective barriers, water retention around roots, and nutrient accumulation. We performed three treatability studies to evaluate the effectiveness of the biopolymer as a soil amendment to increase slope stability and reduce transport of solids in runoff water, reduce the transport of heavy metals associated with suspended sediment from small arms firing ranges, and reduce the generation of dust. Four soil types were used: Silty Sand (SM), Sandy Silt (ML), Silt (S), and Silty Clay (CL). These soil types were selected because they are prone to wind and water erosion thus presenting possible worst case scenarios. The study of sediment transport demonstrated that the biopolymer soil amendment was able to significantly reduce surface water erosion and particulate and heavy metal transport in leachate. The biopolymer soil amendment effectively maintained the slope stability of a simulated berm. In addition, biopolymer added to the Silty Sand soil at 0.5% (w:w) loading rate reduced dust production compared to the control at all relative humidities, indicating it should perform well in both arid and tropical environments.					
15. SUBJECT TERMS Biopolymer Dust		Erosion control Extracellular polymeric substance (EPS) Slope stability Soil additive		Soil stabilization Sustainability Total suspended solids	
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (include area code)
				43	